AD-A226 582

OFFICE OF NAVAL RESEARCH

FTIR STUDIES REVEAL THAT SILICON-CONTAINING LASER-INDUCED DESORPTION PRODUCTS ARE SURFACE REACTION INTERMEDIATES

P.Gupta, A.C. Dillon, P.A. Coon and S.M. George

In Press

Chemical Physics Letters

1990

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
	Approved for public release:
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	Distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Technical Report No. 11	11

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Department of Chemistry Stanford University		Office of Sponsored Projects Stanford University

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Stanford, California 94305-5080	Stanford, California 94305

8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Office of Naval Research		N00014-86-K-0545

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
Chemistry Division 800 N. Quincy Street Arlington, VA 22217-5000	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)

FTIR Studies Reveal that Silicon-Containing Laser-Induced Desorption Products are Surface Reaction Intermediates

12. PERSONAL AUTHOR(S)

P. Gupta, A.C. Dillon, P.A. Coon and S.M. George

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Interim/Technical	FROM _____ TO _____	90/31/07	

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Silicon-containing laser-induced desorption (LID) products such as SiOH and $SiNH_2$ have been observed from Si(111)·7x7 surfaces exposed to H_2O and NH_3. Assuming that the LID species were derived from surface reaction intermediates, these LID products were employed to examine the thermal stability of the SiOH and $SiNH_2$ surface species. Fourier transform infrared (FTIR) transmission spectroscopy was recently utilized to monitor the decomposition of SiOH and $SiNH_2$ surface species following the dissociative adsorption of H_2O and NH_3 on porous silicon surfaces. The FTIR results on porous silicon surfaces were in excellent agreement with the previous LID studies on Si(111)7x7. The correspondence between the FTIR and LID investigations indicated that silicon-containing LID products are derived from silicon surface reaction intermediates. (√s)

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Dr. David L. Nelson / Dr. Mark Ross	(202) 696-4410	

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.
All other editions are obsolete.

FTIR Studies Reveal that Silicon-Containing Laser-Induced Desorption Products are Surface Reaction Intermediates

P. Gupta, A.C. Dillon, P.A. Coon and S.M. George
Chemistry Department
Stanford University
Stanford California 94304

Abstract

Silicon-containing laser-induced desorption (LID) products such as SiOH and $SiNH_2$ have been observed from Si(111) 7x7 surfaces exposed to H_2O and NH_3. Assuming that the LID species were derived from surface reaction intermediates, these LID products were employed to examine the thermal stability of the SiOH and $SiNH_2$ surface species. Fourier transform infrared (FTIR) transmission spectroscopy was recently utilized to monitor the decomposition of SiOH and $SiNH_2$ surface species following the dissociative adsorption of H_2O and NH_3 on porous silicon surfaces. The FTIR results on porous silicon surfaces were in excellent agreement with the previous LID studies on Si(111) 7 X 7. The correspondence between the FTIR and LID investigations indicates that silicon-containing LID products are derived from silicon surface reaction intermediates.

A-1

1

I. Introduction

Laser-induced desorption (LID) has recently been developed as a time-dependent probe of silicon surface processes. LID studies have monitored the desorption kinetics of hydrogen on Si(111) 7x7 (1) and Si(100) 2 X 1 (2) and the adsorption kinetics of molecular O_2 (3) and $SiCl_4$ (4) on Si(111) 7x7. LID investigations have also revealed that silicon-containing species can be desorbed from Si(111) 7x7 after exposure to H_2O, NH_3, CH_3OH and atomic hydrogen (5,6). Assuming that the silicon-containing species were derived from surface reaction intermediates, these LID products were employed to examine the thermal stability of SiOH and $SiNH_2$ species on Si(111) 7x7 after the dissociative adsorption of H_2O (7) and NH_3 (6).

Although silicon-containing LID products may be directly derived from surface reaction intermediates, these species may also be generated by laser-driven processes or reactions in the gas phase. The correlation between silicon-containing LID products and surface species must be established before LID techniques can be used to study silicon surface reaction kinetics. This correlation can not be established with ordinary temperature-programmed desorption (TPD) studies because rapid laser-induced heating rates are required to desorb the silicon-containing species. The relationship between silicon-containing LID products and silicon surface reaction intermediates can be demonstrated using spectroscopic techniques.

Recently, transmission FTIR spectroscopy was utilized to determine the thermal stability of the SiOH and $SiNH_2$ silicon surface species following H_2O (8) and NH_3 (9) exposure, respectively. These transmission FTIR studies were performed in UHV using high-surface-area porous silicon samples. In this letter, the FTIR results for the thermal stability of the SiOH and $SiNH_2$ surface species are compared with the corresponding LID studies on Si(111) 7x7. This comparison indicates that the silicon-containing LID products from Si(111) 7x7 are derived from silicon surface reaction intermediates.

II. Experimental

Previous transmission FTIR studies have demonstrated that high-surface-area porous silicon can be used to monitor sili on surface chemistry (8-10). High-surface-area porous silicon surfaces are required for transmission FTIR spectroscopic studies because single-crystal samples do not have sufficient sensitivity given typical infrared cross sections of $1 \times 10^{-18} \, cm^2$ (10). The electrochemical techniques employed to prepare porous silicon have been described previously (10). Earlier studies have characterized the physical properties of porous silicon (12-14).

The surfaces of porous silicon are passivated with hydrogen after anodization. The infrared spectra of hydrogen on the anodized porous silicon surfaces is very similar to the infrared spectra of hydrogen on Si(100) 2 X 1 (15). Initial studies on porous silicon have explored H_2 desorption from monohydride and dihydride species (10). Desorption kinetics of H_2 from these high surface area silicon surfaces were in agreement with H_2 desorption kinetics obtained from isothermal LID studies on Si(111) 7 X 7 (1,16).

In this study, hydrogen was first desorbed from the anodized porous silicon surfaces in UHV. The porous silicon surfaces were then exposed to H_2O and NH_3 (ND_3) at 300 K until a saturation coverage was obtained. Saturation exposures were typically performed at 1×10^{-5} Torr for 20 - 25 minutes. The porous silicon samples were then heated to progressively higher annealing temperatures for 60 seconds. After each annealing temperature, the FTIR spectra were recorded at 300 K.

FTIR studies were performed in a UHV chamber designed for *in-situ* transmission FTIR studies that has been described elsewhere (8-10). Compared with earlier descriptions (10), a sample introduction chamber and an isolation valve were added to facilate a rapid recovery time after changing samples. A Nicolet 740 FTIR spectrometer was employed in these studies. The infrared beam passed through a pair of 0.5 inch thick CsI windows on the vacuum chamber. The O-ring seals on the CsI salt windows limited the typical base operating pressures in the FTIR chamber to 1×10^{-8} Torr.

For the LID studies, the Si(111) 7x7 were prepared and cleaned as described previously (1,6,7). The Si(111) 7x7 surfaces were then exposed to H_2O and NH_3 (ND_3) at 300 K until a saturation coverage was acheived. LID signals were subsequently obtained during linear temperature ramps of 2 K/sec for both H_2O and ND_3 on Si(111) 7x7.

The experimental apparatus for the LID studies has been described previously (1). Briefly, the ultrahigh vaccum (UHV) chamber maintained a typical base pressure of 4×10^{-10} Torr. For surface analysis, the UHV chamber was equipped with a low-energy diffraction (LEED) spectrometer and a cylindrical mirror analyzer for Auger electron spectroscopy (AES). An Exrel C-50 quadropole mass spectrometer was used for the laser-induced desorption (LID) experiments. The TEM-00 Q-switched Ruby laser employed in these LID studies had a temporal width of 100-120 nsec (FWHM) and a Gaussian spatial profile (1).

III. Results

A. H_2O Decomposition

The FTIR spectrum shown in Fig. 1 was obtained after a saturation H_2O exposure on porous silicon at 300 K (8). This infrared spectrum shows the silicon hydride and silicon hydroxyl dissociation products following H_2O adsorption, i.e. $H_2O \rightarrow SiH + SiOH$. The silicon hydride and silicon hydroxyl species were characterized by the Si-H stretching vibration at 2090 cm^{-1} and the SiO-H stretching vibration at 3680 cm^{-1}. These assignments are in agreement with previous EELS experiments of H_2O on Si(111) 7x7 (17,18).

Figure 2 shows the change in the infrared spectrum of the SiO-H and Si-H stretching vibrations as a function of annealing temperature (8). Figure 2a displays the decrease in the absorbance of the SiO-H stretching vibration as the surface is annealed from 300 K to 640 K. Figure 2b displays the increase in the absorbance of the Si-H stretching vibration as the surface is annealed over the same temperature range.

Figure 3a displays the normalized integrated absorbance of the SiO-H and the Si-H stretching vibrations versus annealing temperature. The SiOH surface species has decomposed by

620K (8). Figure 3a also demonstrates that the SiH surface species increases by a factor of approximately 2 as the annealing temperature is increased from 300 K to 650 K. Above 650 K, the integrated absorbance for the Si-H stretching vibration decreases. This decrease is consistent with the thermal desorption of H_2 from silicon surfaces (1,10,16,19).

The growth of surface silicon oxide has also been monitored by examining the absorbance of a Si-O-Si assymetric stretch at 950 cm^{-1} (8). The absorbance of the Si-O-Si stretch grows concurrently with the absorbance of the Si-H stretch. The increase of the integrated absorbance of both the Si-O-Si and Si-H stretching vibrations is caused by the decomposition of surface SiOH species to produce surface SiH and SiOSi species, i.e. SiOH →SiH + SiOSi.

Following a saturation H_2O dose on Si(111) 7x7 (7), LID studies of H_2O decomposition on Si(111) 7x7 observed H_2 and SiO thermal reaction products and a silicon-containing SiOH LID product at m=45 amu. These results suggested that rapid LID heating rates were able to desorb surface reaction intermediates that could not be desorbed at slower heating rates (20,21). The temperature dependence of the LID signals for H_2 and SiOH are shown in Fig. 3b after a saturation H_2O exposure on Si(111) 7x7 (7) at 110K.

Figure 3b reveals that the SiOH LID signal decreases progressively between 400 and 600 K. These SiOH LID results are in close agreement with the SiOH FTIR results shown in Fig. 3a. Fig. 3b also shows a progressive rise in the H_2 LID signal with surface temperature. Seperate LID experiments with hydrogen on Si(111) 7x7 indicated that this behaviour results primarily because of the temperature dependence of the LID signals (22,23). The decrease of the H_2 LID signal at 800 K is consistent with the thermal desorption of H_2 from Si(111) 7x7 (1,16,19).

B. NH3 Decomposition

Figure 4 displays the FTIR spectra after a saturation dose of NH_3 on porous silicon at 300 K. The infrared features at 1534 cm^{-1} and 2077 cm^{-1} are assigned to the SiN-H_2 scissors mode and the Si-H stretching vibration, respectively (9). The FTIR spectra suggests that NH_3 dissociative chemisorption on silicon surfaces occurs as NH_3 → SiH + SiNH_2. These assignments

5

are in agreement with previous EELS studies of NH_3 on Si(111) 7x7 (24) and gas-phase infrared studies of substituted aminosilanes, R_3SiNH_2 (25).

Figure 5 displays the change in the infrared spectrum of the $SiN-H_2$ scissors mode and the Si-H stretching vibration as a function of annealing temperature (9). Figure 5a shows the decrease in the absorbance of the $SiN-H_2$ scissors mode as the surface is annealed from 300 K to 680K. Figure 5b shows a broadening and increase in the absorbance of the Si-H stretching vibration as the surface is annealed in the same temperature range.

Figure 6a displays the normalized integrated absorbance of the $SiN-D_2$ scissors mode and the Si-D stretching vibration versus annealing temperature (9). The integrated absorbance of the $SiN-D_2$ scissors mode indicates that the $SiNH_2$ surface species has decomposed by 700 K. ND_3 was employed in Fig. 6 because a small SiO contamination interfered with the $SiNH_2$ LID signal at m=44 amu and prevented an accurate comparison of FTIR and LID results. The increase of the integrated absorbance of the Si-D stretching vibration is attributed to the decomposition of $SiND_2$ species to produce SiD species, i.e. $SiND_2 \rightarrow 2SiD + Si_3N$. Above 650K, the decrease of the absorbance of the Si-D stretching vibration is caused by the desorption of D_2 from the silicon surface (1, 10, 16, 19).

A variety of LID signals were observed from the Si(111) 7x7 surface following a saturation NH_3 exposure at 110K (6). Besides a large H_2 LID signal, $SiNH_2$ and SiNH LID signals were observed at m= 44 and m=43. These LID signals were used to monitor the thermal stability of hydrogen and $SiNH_2$ species on the Si(111) 7x7 surface in temperature-programmed LID experiments (6).

The temperature dependence of the LID signals for D_2 and $SiND_2$ is shown in Fig. 6b. The $SiND_2$ LID signal decreased slowly between 400 and 700 K (6). These $SiND_2$ LID results are in very good agreement with the $SiND_2$ FTIR results shown in Fig. 6a. The D_2 LID signal increases with surface temperature until D_2 desorbs from the Si(111) 7x7 surface at 800 K (1).

IV. Discussion

LID and FTIR techniques are useful probes of silicon surface chemistry. LID is easily applied to single-crystal surfaces, but must observe products after they have desorbed from the surface. Transmission FTIR can observe surface species, but must be applied to high surface area samples for sufficient sensitivity. The association between silicon-containing LID species and surface reaction intermediates was a suggestion from the LID studies (5-7). This comparison of LID and FTIR results for H_2O and NH_3 decomposition on Si(111) 7x7 and porous silicon surfaces was performed to test this hypothesis.

Previous EELS studies of H_2O absorption on Si(111) 7x7 surfaces (17,18) and reflectance infrared studies of water on Si (100) 2 X 1 (26) surfaces have observed SiO-H and Si-H stretching modes in agreement with Fig. 1. The dissociative adsorption of H_2O to produce SiH and SiOH on silicon surfaces has been fairly well established (8). The temperature-dependent decomposition of SiOH species and growth of SiH species monitored in Fig. 3a is also consistent with the reaction SiOH $\rightarrow$ SiH + SiOSi. In particular, the twofold increase of the absorbance of the Si-H stretching vibration argues for an overall reaction of SiH + SiOH $\rightarrow$ 2 SiH + SiOSi.

The correlation is excellent between the integrated absorbance of the SiO-H stretching vibration and the SiOH LID products versus temperature shown in Figs. 3a and 3b. If the laser was dictating the reaction products or if reactions in the gas phase were producing the silicon-containing LID products, this correpondence between the temperature dependence of the SiOH LID signal and the SiO-H infrared absorbance would not be expected. This correlation argues that the SiOH LID products from Si(111) 7x7 are derived from SiOH silicon surface species.

The dissociative adsorption of NH_3 (ND_3) to produce SiH and $SiNH_2$ on silicon surfaces has been suggested by several studies (6, 9). In agreement with Fig. 4, previous EELS studies of NH_3 and ND_3 adsorption on Si(111) 7x7 have observed the $SiN-H_2$ ($SiN-D_2$) scissors mode and the $SiN-H_2$ ($SiND_2$) and Si-H stretching modes (24). The temperature-dependent decomposition of the $SiNH_2$ species and growth of the SiH species monitored in Fig. 5 also suggests the

7

conversion of $SiNH_2$ species to surface hydrogen species. Instead of the threefold increase expected if $SiH + SiNH_2 \rightarrow 3 SiH + Si_3N$, the absorbance of the Si-H stretching vibration increases approximately twofold. The recombinative thermal desorption of NH_3 may explain this smaller increase (27).

The correlation is extremely good between the integrated absorbance of the SiN-D_2 scissors mode and the $SiND_2$ LID signal displayed in Figs. 6a and 6b. Both the integrated absorbance of the SiN-D_2 scissors mode and the $SiND_2$ LID products decrease between 450 -700 K. Very similar results are observed when comparing the temperature dependence of the integrated absorbance of the SiN-H_2 scissors mode and the $SiND_2$ LID signal (6). The close correspondence between the LID and FTIR results shown in Fig. 6 argues that the LID $SiNH_2$ products are derived from $SiNH_2$ surface species.

These FTIR results add to the accumulating evidence that rapid laser heating rates of 10^{10} -10^{11} K/sec can induce the desorption of many surface reaction species that normally would react at slower heating rates (20,21). For example, in addition to SiOH and $SiNH_2$ LID products from H_2O and NH_3 adsorbed on Si(111) 7x7, $SiOCH_3$ is also observed from CH_3OH/Si(111) 7 X 7 (5). Likewise, at higher hydrogen coverages when the β_2 H_2 -TPD peak corresponding to dihydride surface species is present (1, 10), SiH_x is detected as a LID product from Si(111) 7x7 (5).

On metal surfaces, there are numerous examples of LID products that have been observed that would have reacted at slower heating rates. For example, CH_3OH has been observed in the LID yield from CH_3OH/Ni(100) (28, 29) and CH_3OH/Ru(001) (30, 31). Likewise, C_2H_4 has been detected as an LID product from C_2H_4 adsorbed on Ni(100) (20) and Pt (111) (32).

The appearance of these LID products at rapid laser heating rates can be explained by the competition between desorption and reaction pathways (20, 21). In particular, many adsorbed reactants have desorption and reaction kinetics where the preexponential and activation barrier for desorption are both larger than the preexponential and activation barrier for reaction. In this case,

8

the rapid heating rates typically used in LID experiments will generally change the yield from reaction-dominated at slow heating rate to desorption-dominated at rapid heating rate (20,21). Inefficient thermal coupling between the surface and the reactants may also enhance the desorption pathway (33,34).

The ability to desorb surface reaction intermediates is extremely valuable for surface kinetic studies. In addition to the decomposition of SiOH (7) and $SiNH_2$ (6) on Si(111) 7x7, methanol decomposition on Ni(100) (28, 29) and Ru(001) (30, 31), ethylene decomposition on Ni(100) (20) and Pt(111) (32) and cyclohexane decomposition on Pt(111) (35) have all been studied using LID techniques. Because there is an excellent correlation between the silicon-containing LID products and surface reaction intermediates, these silicon-containing species should have general utility as a probe of reaction intermediates on silicon surfaces.

V. Conclusions

Silicon-containing laser induced desorption (LID) products such as SiOH and $SiNH_2$ have been observed from Si(111) 7x7 surfaces exposed to H_2O and NH_3. Assuming that the silicon-containing LID species were derived from surface reaction intermediates, these LID products were used to examine the thermal stability of the SiOH and $SiNH_2$ surface species. At saturation coverage, the SiOH and $SiNH_2$ surface species were both observed to decompose slowly over a wide temperature range from 400 K - 600 K.

In complementary studies, Fourier transform infrared (FTIR) transmission spectroscopy was used to monitor the decomposition of H_2O and NH_3 on porous silicon surfaces. The FTIR spectra observed SiOH and $SiNH_2$ surface species following the dissociative adsorption of H_2O and NH_3. The FTIR results for the thermal stability of the SiOH and $SiNH_2$ surface species were in excellent agreement with the previous LID studies on Si(111) 7 X 7. The correspondence between the FTIR and LID investigations indicates that silicon-containing LID products are derived from silicon surface reaction intermediates.

VI. Acknowledgements

References

1. B.G. Koehler, C.H. Mak, D.A. Arthur, P.A. Coon and S.M. George, J. Chem. Phys. **89** 1709 (1988).

2. K. Sinniah, M.G. Sherman, L.B. Lewis, W.H. Weinberg, J.T. Yates, Jr. and K.C. Janda, J. Chem. Phys. **92** 5700 (1990).

3. P. Gupta, C.H. Mak, P.A. Coon and S.M. George, Phys. Rev. B **40** 7739 (1989).

4. P.Gupta, P.A. Coon, B.G. Koehler and S.M. George, J. Chem. Phys. *in press*.

5. C.H. Mak, B. G. Koehler and S.M. George, Surf. Sci. Lett. **208** L42 (1989).

6. B.G. Koehler, P.A. Coon and S.M. George, J. Vac. Sci. Technol. **B7** 1303 (1989).

7. B.G. Koehler, C.H. Mak and S.M. George, Surf. Sci. **221** 565 (1989).

8. P. Gupta, A.C. Dillon, A.S. Bracker and S.M. George, *submitted to Surf. Sci.*

9. A.C. Dillon, P. Gupta, M.B. Robinson and S.M. George, *in preparation*

10. P. Gupta, V.L. Colvin and S.M. George, Phys. Rev. B **37** 8234 (1988).

11. L.A. Pugh and K.N. Rao, *Molecular Spectroscopy: Modern Research* edited by K.N. Rao (Academic, NY, 1976) Vol II.

12. M.I. J. Beale, N.G. Chew, M.J. Uren, A.G. Cullis and J.D. Benjamin, Appl. Phys. Lett **46** 86 (1985).

13. K. Barla, R. Herino, G. Bomchil and T.C. Pfister, J. Cryst. Growth **68** 727 (1984).

14. I.M. Young, M.I.J. Beale and J.E. Bejamin, Appl. Phys. Lett. **46** 1133 (1985).

15. Y.J. Chabal and K. Raghavachari, Phys. Rev. Lett. **54** 1055 (1985).

16. B.G. Koehler, P. Gupta, P.A. Coon, M. Wise and S.M. George, (in preparation).

17. M. Nishijima, K. Edamoto, Y. Kubota, S. Tanaka and M. Onchi, J. Chem. Phys. **84** 6458 (1986).

18. H. Ibach, H. Wagner and D. Bruchmann, Sol. State Commun. **42** 457 (1982).

19. G. Schulze and M. Henzler, Surf. Sci. **124** 336 (1983).

20. R. B. Hall, J. Phys. Chem. **91** 1007 (1987).

21. A.A. Deckert and S.M. George, Surf. Sci. **182** L215 (1987).

22. B.G. Koehler and S.M. George, *submitted to Surf. Sci.*

23. J.L. Brand and S.M. George, Surf. Sci. **167** 341 (1986).

24. S. Tanaka, M. Onchi and M. Nishijima, Surf. Sci. **191** L756 (1987).

25. A. Marchand, M.T. Forel, F. Metras and J. Valade, J. Chim. Phys. **61** 343 (1964).

26. Y.J. Chabal, Phys. Rev. B **29** 3677 (1984).

27. M.J. Dresser, P.A. Taylor, R.M. Wallace, W.J. Choyke and J.T. Yates, Jr., Surf. Sci. **218** 75 (1989).

28. R.B. Hall and A.M. DeSantolo, Sur. Sci. **137** 421 (1984).

29. R.B. Hall, A.M. DeSantolo and S.J. Bares, Surf. Sci. **161** L533 (1985).

30. A.A. Deckert, J.L. Brand, C.H. Mak, B.G. Koehler and S.M. George, J. Chem. Phys. **87** 1936 (1987).

31. A.A. Deckert, J.L. Brand, M.V. Arena and S.M. George, Surf. Sci. **226** 42 (1990).

32. C.L. Pettiette-Hall, D.P. Land, R.T. McIver, Jr. and J.C. Hemminger, J. Phys. Chem. **94** 1948 (1990).

33. R.N. Zare and R.D. Levine, Chem. Phys. Let. **136** 593 (1987).

34. T.A. Holme and R.D. Levine, Surf. Sci. **216** 587 (1989).

35. D.P. Land, C.L. Pettiette-Hall, R.T. McIver, Jr. and J.C. Hemminger, J. Am. Chem. Soc. **111** 5970 (1989).

Figure Captions

1. Infrared spectrum after a saturation H_2O exposure on porous silicon surfaces at 300K.

2. Infrared absorbance as a function of annealing temperature after a saturation H_2O exposure at 300 K for a) the SiO-H stretching vibration and b) the Si-H stretching vibration.

3. a) Integrated infrared absorbances of the SiO-H and Si-H stretching vibrations at 3680 cm^{-1} and 2090 cm^{-1}, respectively, versus annealing temperature after a saturation H_2O exposure on porous silicon surfaces at 300 K.
    b) LID signals for H_2 and SiOH during a linear temperature ramp at 2 K/s following a saturation H_2O exposure on Si(111) 7x7 at 110 K.

4. Infrared spectrum after a saturation NH_3 exposure on porous silicon surfaces at 300 K.

5. Infrared absorbances as a function of annealing temperature after a saturation NH_3 exposure at 300 K for a) the SiN-H_2 scissors vibration and b) the Si-H stretching vibration.

6. a) Integrated infrared absorbances of the SiN-D_2 scissors and the SiD stretching vibrations at 1534 cm^{-1} and 2077 cm^{-1}, respectively, versus annealing temperature after a saturation ND_3 on porous silicon surfaces at 300 K.
    b) LID signals for D_2 and SiND$_2$ during a linear temperature ramp at 2 K/s following a saturation ND_3 exposure on Si(111) 7x7 at 110 K.
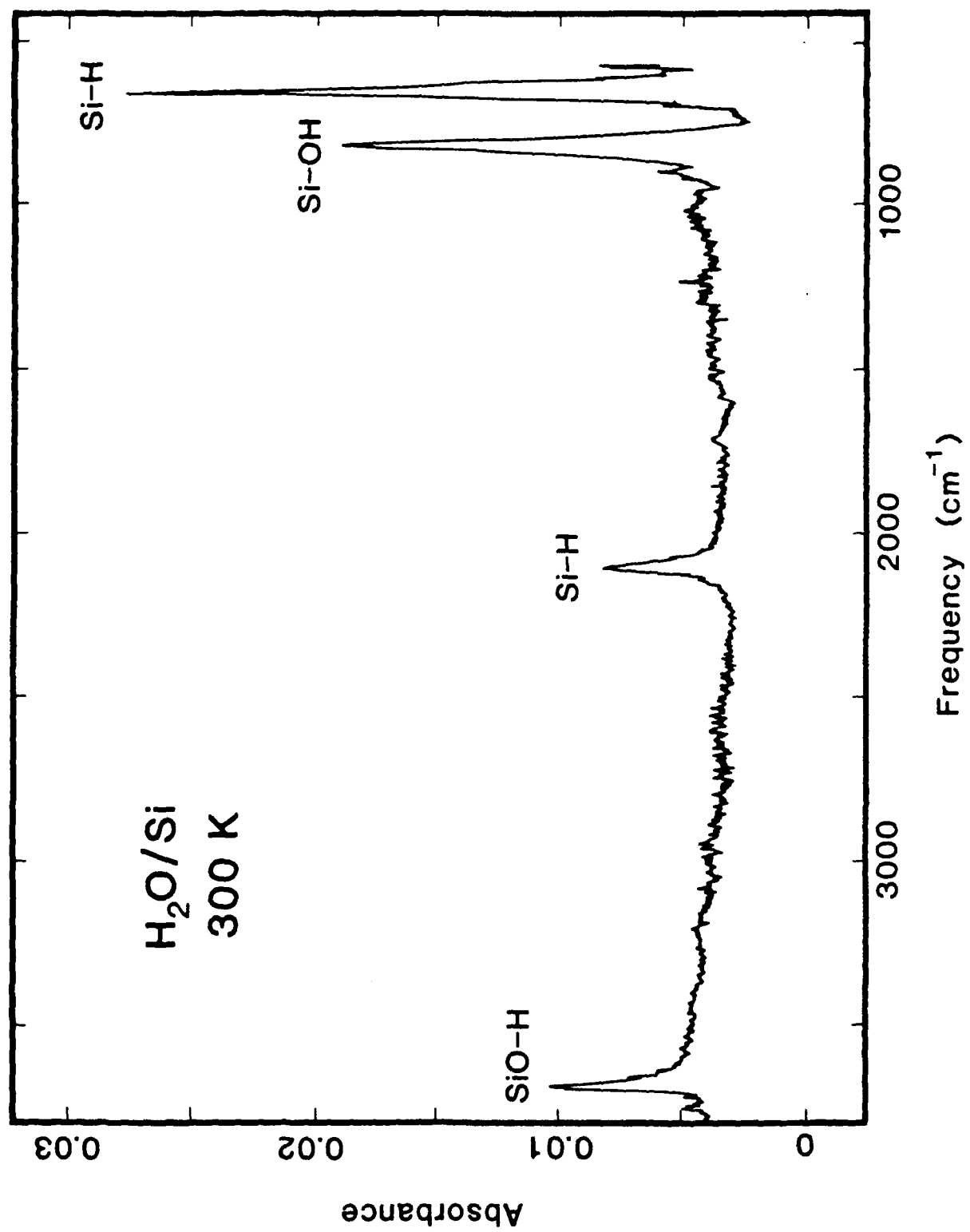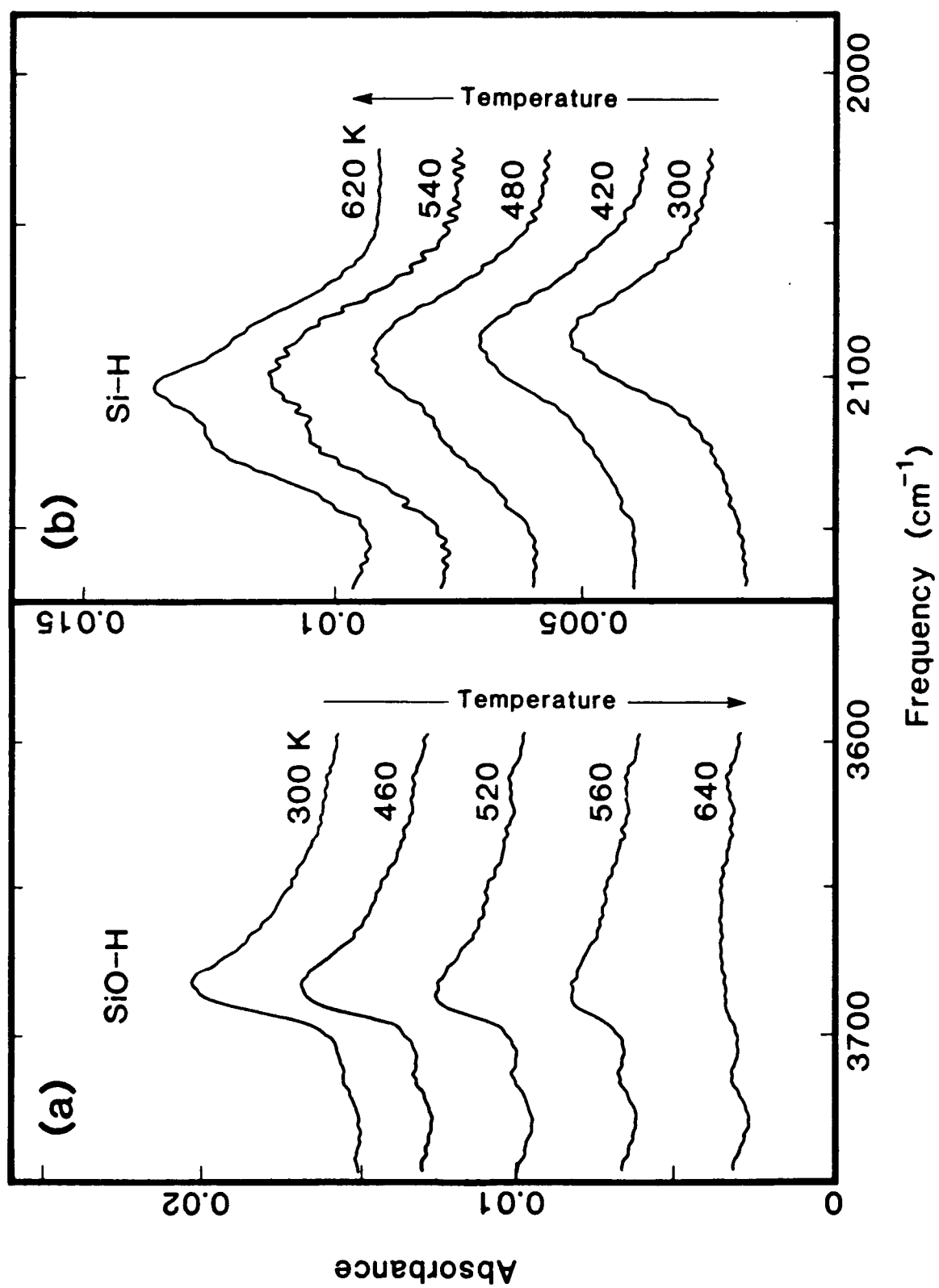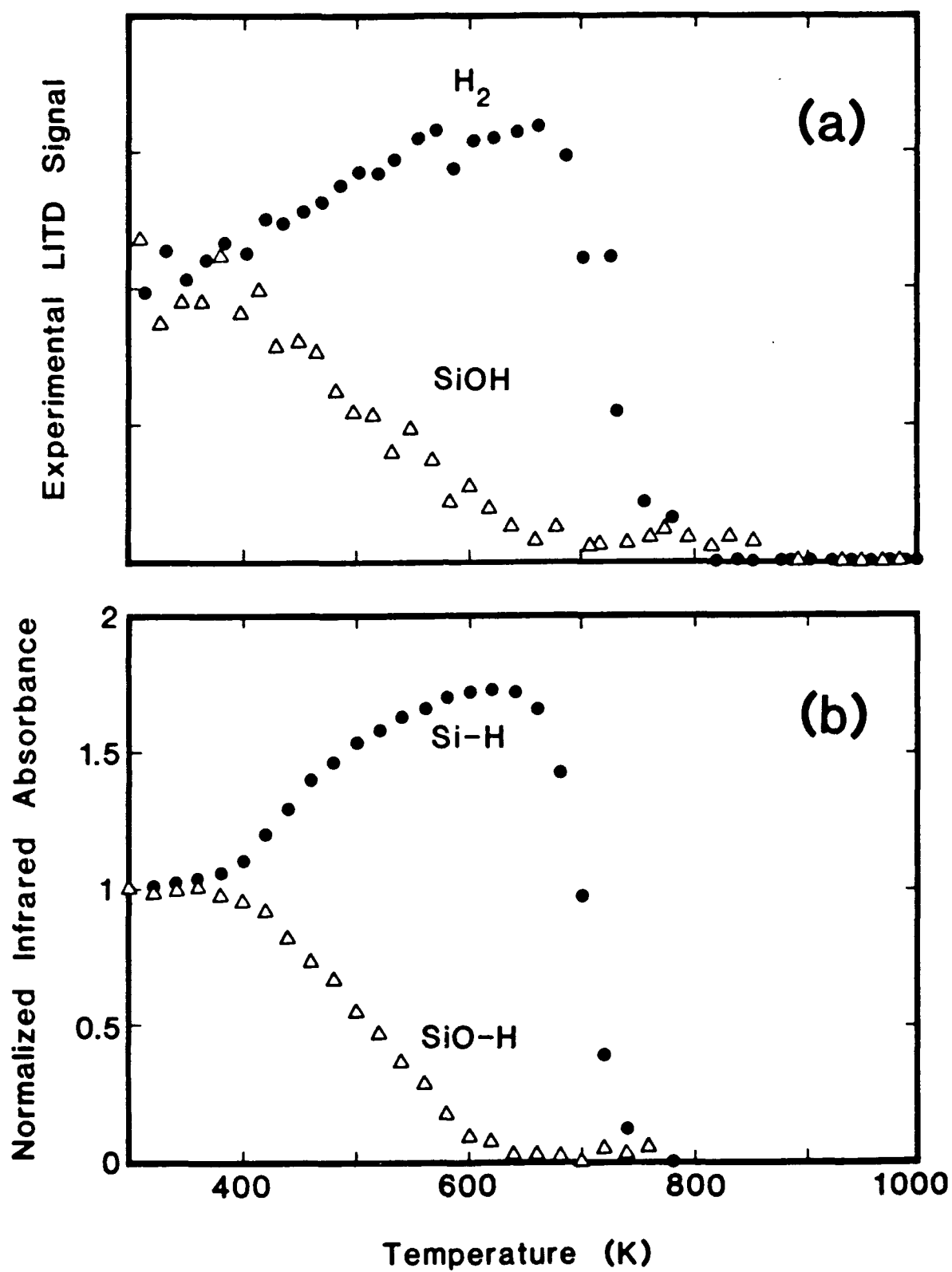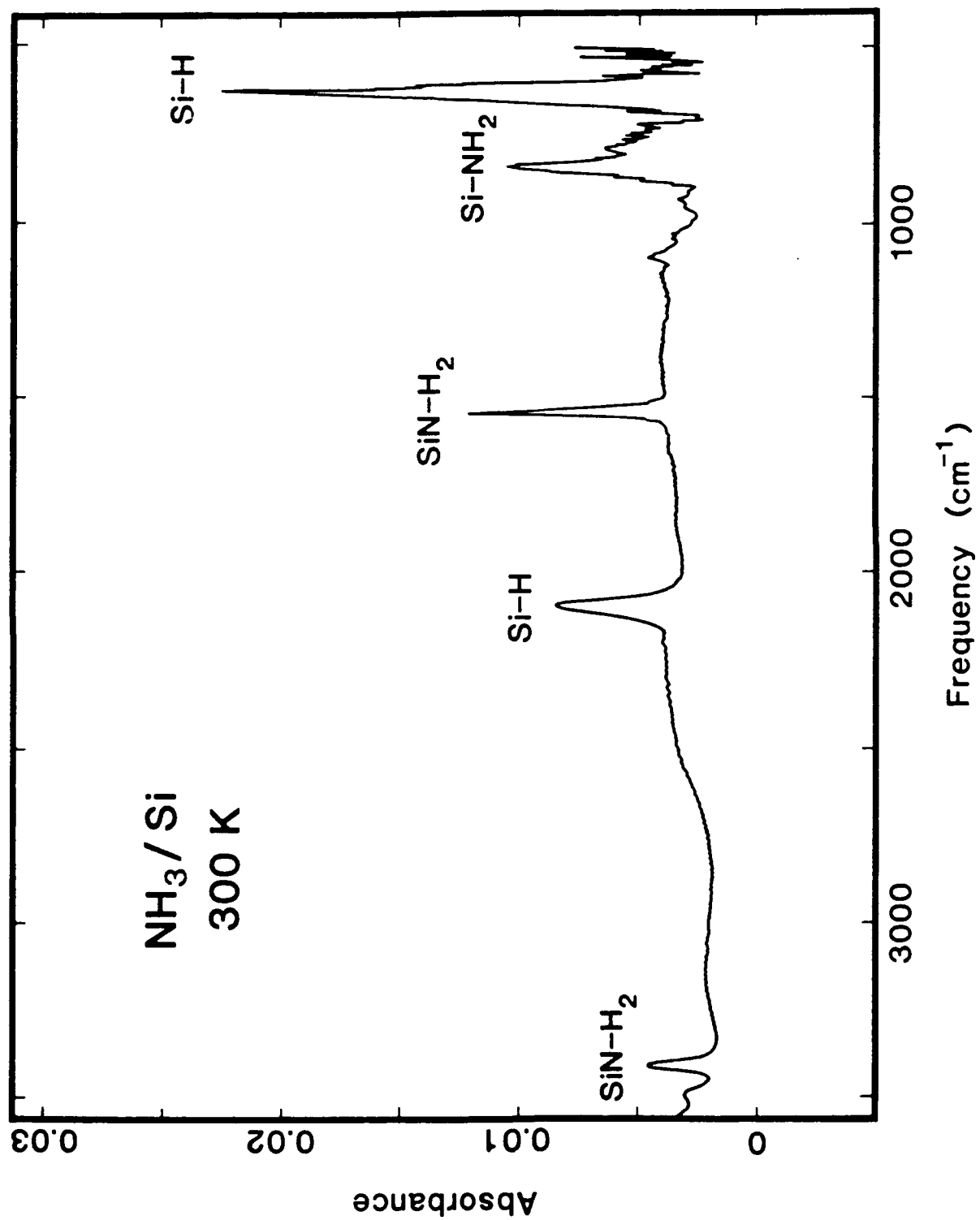
H₂O/Si
300 K

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6